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(54) **Process for the preparation of very fine glass powder of high purity**

(57) In the process glass powder having a maximum particle size of ≤ 300 μm is ground to the desired mean particle size d_{50} of ≤ 10 μm in a stirred mill by means of grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder, in the presence of a grinding liquid comprising water or a mixture of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule. The grinding slurry is then frozen, and the solvent is subsequently removed from the grinding slurry by freeze-drying. The glass powder can be prepared with mean particle sizes d_{50} of up to 0.2 μm and is particularly suitable as a filler for dental plastics.

The grinding elements may be cylindrical. Various organic compounds are detailed and pH values of the grinding liquid are specified.

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Process for the Preparation of Very Fine Glass Powder of High Purity

This invention relates to a process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of ≤ 10 µm by wet-grinding in the presence of grinding elements.

High-purity glass powders are required, in particular, as fillers for plastics employed in the dental sector, for example dental fillings. For glass powders of this type, mean particle diameters d_{50} of at most 10 µm, preferably < 5 µm, in particular ≤ 3 µm are required since the mechanical properties, such as polishability and abrasion resistance, are improved with increasing fineness (decreasing particle diameter). Excessively large glass particles (>10 µm) produce a rough surface in the cured plastics or break out and leave holes and sharp edges. The refractive index of the glass powder must agree very closely with that of the plastics in order to achieve high transparency and translucency of the filled plastics. If the glass powder contains, for example, colouring particles and/or particles having different refractive indices, the translucency and transparency and possibly also the colour of the filled plastics are impaired, so that the plastics can frequently only be used with considerable restrictions, if at all.

Glass powders are prepared by grinding. The grinding processes hitherto have the disadvantages of, in some cases, high energy consumption for the grinding, long grinding times for fine particle sizes and high abrasion of grinding pebbles and the mill wall. The particles produced by such abrasion can impair the transparency and translucency of the filled plastics and make the

production of very pale tooth colours difficult. The conventional dry-grinding processes are at the limit of their performance for these small particle sizes, require long grinding times and generally require an additional air separator for classifying the grinding material. Abrasion of the grinding elements, wear of the grinding container or of the air separator and the energy consumption are so high that these grinding processes are unsuitable for the preparation of very fine glass powders.

Although wet-grinding processes using water give fine particle sizes in a shorter time than do dry-grinding processes, the grinding elements are still subject to considerable abrasion, and a particular disadvantage is that numerous agglomerates (i.e. very solid clusters of powder particles which act in a similar way to large individual particles and dramatically impair the properties of the filled plastics) form from the grinding slurry on drying. If, by contrast, the grinding is carried out in the presence of organic liquids in which agglomeration is substantially suppressed on drying (for example low-boiling hydrocarbons), the grinding times are considerably extended, the amount of grinding abrasion increases correspondingly and additional safety precautions, for example explosion protection, become necessary.

An object of the invention is to provide a process for the preparation of very fine glass powder of high purity in which the grinding operation can be carried out in a relatively short time and with a low consumption of energy and in which mean particle sizes d_{50} of from 0.2 to 10 μm, preferably from 0.5 to 5 μm, in particular from 0.5 to 2 μm, can be produced and in which a glass powder having a purity which allows even the preparation of filled plastics which give very pale tooth colours in the

dental sector can be obtained.

According to the present invention, there is provided a process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of ≤ 10 μm, said process comprising the steps of grinding a glass powder having a maximum particle size of ≤ 300 μm to the desired particle size in a stirred mill using grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder, in the presence of a grinding liquid comprising water or a mixture of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule; freezing the resultant grinding slurry; and subsequently removing the grinding liquid from the grinding slurry by freeze-drying.

The process is carried out using a stirred mill (attrition mill eg an Attritor mill) since a mill of this type allows glass powders having the desired fineness to be prepared particularly simply. In order to achieve short grinding times, it is furthermore necessary to carry out the grinding in the presence of a grinding liquid comprising water or a mixture of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule. Suitable organic compounds are aldehydes (eg formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and pentanaldehyde), ketones (eg acetone, methyl ethyl ketone and diethyl ketone), esters (eg ethyl acetate, methyl acetate, propyl acetate, methyl formate, ethyl formate and propyl formate) or acids (eg carboxylic acids such as acetic acid and propionic acid). Monohydric, dihydric and trihydric alcohols are also suitable. An example of a suitable trihydric alcohol is glycerol, but this requires long evaporation times; examples of suitable dihydric alcohols are ethylene

glycol and the propanediols. Monohydric alcohols, in particular those having up to five carbon atoms in the molecule, are particularly suitable. Mixtures of water with organic compounds are preferred since the attack of water on the glass powder is less pronounced. Of the eight isomeric pentanols, most can only be used in admixture with lower alcohols since their water solubility is inadequate up to 2-pentanol. Their use is also associated with disadvantages due to the in some cases unpleasant odour. Of the four isomers of butanol, some are likewise only moderately soluble in water and so can also only be used in admixture with other alcohols. However, t-butyl alcohol is highly suitable, both due to its good water solubility and also due to its high melting point.

Of the organic compounds, those are preferred whose boiling point is not above 100°C, since otherwise removal from the grinding slurry during drying takes too long. Particularly preferred in this respect are acetone, t-butyl alcohol, methanol, ethanol, n-propanol and i-propanol. Particularly good grinding results are achieved using mixtures of one or more of these alcohols and acetone with from 80 to 99% weight of water. The proportion of water in the mixture should preferably be selected so that the mixture has a freezing point of above -40°C since the operating costs for freezing equipment which operates at lower temperatures is disproportionately high.

It has furthermore proved advantageous for the grinding operation to be carried out within a pH range of from 1 to 12. Acid or alkaline attack on the glass can take place outside these limits. It is particularly advantageous to work either in the acidic range, i.e. at a pH of from 1 to 6, in particular from 3 to 6, or in the alkaline range, i.e. at a pH of from 8 to 12, in

particular 8 to 11. At these pH values, the viscosity of the grinding slurry drops to lower values. A lower slurry viscosity means that the amount of energy used to comminute the glass, as a proportion of the total grinding energy expended, becomes proportionally higher and the amount used for "stirring" the slurry becomes proportionally lower, so that the grinding performance increases. The pH can be adjusted using any desired acids and bases so long as they react with the glass only to a slight extent, or not at all. However, preference is given to acid and bases which can also easily be removed again from the grinding slurry, eg readily volatile acids and bases, such as acetic acid, HCl, HNO_3, NH_3, methylamine, dimethylamine, ethylamine, diethylamine etc. Preference is given to HCl, HNO_3, NH_3 and ethylamine.

In order to avoid impairing the properties of the resultant glass powder with regard to colour, transparency and translucency in the processed state, grinding elements made of a glass whose abrasion impairs the properties of the resultant glass powder only insignificantly, or not at all, are employed. Optical and mechanical properties, such as refractive index, colour, hardness, resistance to hydrolysis, polishability, etc., of the glass employed for the grinding elements should be similar or preferably identical to the corresponding properties of the glass to be ground. If is preferred for the grinding elements and the glass to be ground to have the same composition.

For grinding in the stirred mill (eg Attritor mill), the material to be ground must be precomminuted to a maximum particle size of ≤ 300 µm, preferably ≤ 200 µm. This precomminution can expediently be effected by dry-grinding of the glass in a ball mill, in which these

particle sizes can be produced rapidly and without measurable abrasion of the grinding container and the grinding balls.

The fine grinding of the precomminuted glass powder to the desired size in the stirred mill is preferably effected using grinding elements having a size of from 0.3 to 10 mm. If the grinding elements are larger than 10 mm, the resultant grinding times may be very long and the wear of the grinding elements and of the mill may also increase considerably. During grinding in the stirred mill, it is preferred for the glass to be ground is pumped through the mill as a slurry (suspension), and for the grinding elements to be retained in the mill by appropriate means, for example by a filter cartridge or a friction gap of appropriate dimensions. If the grinding elements are smaller than 0.3 mm, there is a danger of them no longer being adequately retained and damaging the retention systems.

The number of grinding elements affects the grinding action and thus the grinding time necessary in order to prepare a powder having a certain particle size. At a constant grinding element:grinding material weight ratio, the number of grinding elements, and thus the number of contact points between which the glass particles are ground, increases with decreasing size, and the grinding time drops. Grinding elements having a size of from 0.5 to 2 mm are therefore preferred. The grinding elements may be in the form of balls, cylindrical elements or glass fragments. A cylindrical shape is preferred since this shape allows an optimum grinding result to be achieved. These grinding elements can be obtained from sections of a suitable glass rod or by sintering preforms dry-pressed or extruded from glass powders. The size is taken to mean the diameter in the case of spherical grinding elements and the particle size in the case of

glass fragments. The length, width and height of cubic and similar elements and the diameter and length of cylindrical elements should be within said sizes. In the case of these elements, it is preferred for the elements to be as compact as possible, i.e. for the individual dimensions to be substantially identical.

In stirred mills, the grinding container, the stirrer and other abrasion-endangered parts are generally lined with or comprise metal, in particular hard metal, or abrasion-resistant ceramic, for example Al_2O_3, or porcelain. However, abrasion of the ceramic impairs the translucency and transparency of filled resin compositions prepared using these powders, while metal abrasion can even result in a grey coloration. It is therefore preferred to produce these mill parts from the glass to be ground or from a glass which has similar properties or to coat them with a glass of this type or with an abrasion-resistant, solvent-resistant plastic. The mechanical durability of the plastic coating can be improved by reinforcement with glass powders or glass fibres, which preferably comprise the glass to be ground or a similar glass. Suitable plastics from the group comprising the polyurethanes, aramides or chlorofluorocarbon resins are known per se for lining mills.

When the glass powder has been ground to the desired fineness, the glass slurry is frozen and freeze-dried. During the freeze-drying, the frozen solvent is evaporated in a high vacuum by sublimation. The freeze-drying is well known per se, and freeze-drying units are commercially available from numerous manufacturers. Since the cost of freeze-drying units increase considerably with operating temperatures of below -40°C, solvents or solvent mixtures which are already frozen at temperatures down to -40°C are preferred. After the freeze-drying, the glass powder is in finely divided form

without agglomeration and is ready to use per se.

However, residues from plastic abrasion of the mill lining or from the solvents used may be present in the glass powder, in some case adsorbed very strongly by the glass surface and this sometimes results in the resultant glass powder being unusable for very pale tooth colours. In such cases, also very generally, if extremely pure glass powders are to be produced, the glass powder is heated, after the freeze-drying, for from 1 hour to 10 days in an oxidising atmosphere, i.e. normally in air, at temperatures between 250°C and the glass transition temperature T_g of the glass powder, during which the organic constituents are oxidised. The heating time depends on the temperature to which the glass powder is heated and on the strength with which the organic constituents are adsorbed by the glass powder, and should expediently be matched to the particular grinding conditions. Good results are generally obtained using treatment times of from 12 to 48 hours at from 400 to 600°C.

The process which has been found allows very pure glass powders having mean particle sizes d_{50} of from 0.2 to 10 µm to be produced without difficulty, the particle sizes being determined, for example, using laser diffraction or sedimentation methods (DIN 66 111). Glass powders of this type are suitable for the production of sintered glass ceramics, but in particular in dental technology for the production of filled synthetic resins; for this application, the surface of the glass powder particles is very often treated in a manner known per se with suitable silanes, for example chlorosilanes, in order to obtain better mechanical and chemical binding of the glass powder into the resin composition. Synthetic resins in dental technology are preferably filled with glass

powders having mean particle sizes of from 0.5 to 3 µm, in particular from 0.5 to 1.5 µm. Although the process also allows mean particle sizes of less than 0.2 µm to be produced, the grinding advance in this range is, however, only small, so that the grinding operation is very lengthy and in general is no longer economically worthwhile.

Example

20 kg of glass powder having a particle size of less than 200 µm and 30 litres of suspension liquid (95 wt% water and 5 wt% i-propanol) is introduced into a stirred vessel and pumped continuously through a stirred ball mill which has a capacity of 12.5 litres and which has been previously filled with a grinding medium consisting of 18 kg of glass particles of cylindrical shape having a diameter of 1.3 mm and a length of 1.3 mm. The grinding medium is prevented from leaving the stirred ball mill by providing a gap of 0.3 mm within the mill through which the material passes on its way out of the mill. The impeller of the mill stirs the media at a rate of 1400 revs/minute. The impeller and the interior of the vessel have a resilient coating of a polyurethane resin. After an operation time of 8 hours, the slurry is freeze dried at -40°C. The resultant powder has a grain size of d_{50} = 0.7 µm, d < 3 µm, and is ready for use.

If required, this glass powder may be heated in an oxidizing atmosphere (air) at 500°C to give an extremely pure and bright powder.

CLAIMS

1. A process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of ≤ 10 µm, said process comprising the steps of grinding a glass powder having a maximum particle size of ≤ 300 µm to the desired particle size in a stirred mill using grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder and in the presence of a grinding liquid comprising water or a mixture of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule; freezing the resultant grinding slurry; and subsequently removing the grinding liquid from the grinding slurry by freeze-drying.

2. A process according to Claim 1, wherein the grinding elements have the same composition as the glass to be ground.

3. A process according to Claim 1 or 2, wherein the grinding elements have a size of from 0.3 to 10 mm.

4. A process according to Claim 3, wherein the grinding elements have a size of from 0.5 to 2 mm.

5. A process according to any preceding Claim, wherein the grinding elements are cylindrical.

6. A process according to any preceding Claim, wherein the grinding liquid has a pH of from 1 to 12.

7. A process according to Claim 6, wherein the grinding liquid has a pH of from 2 to 6 or from 8 to 12.

8. A process according to Claim 6 or 7, wherein

hydrochloric acid, nitric acid, ammonia or ethylamine is used to adjust the pH of the grinding slurry.

9. A process according to any preceding Claim, wherein the grinding liquid is a mixture of 80 to 99% by weight water and at least one of methanol, ethanol, n-propanol, i-propanol, acetone and t-butyl alcohol.

10. A process according to any preceding Claim, wherein, in the stirred mill, those parts which come into contact with the material to be ground comprise, or are coated with, an abrasion-resistant plastics or a glass which has the same or similar properties as the glass to be ground.

11. A process according to Claim 10, wherein said abrasion-resistant plastics contains glass powder and/or glass fibres which have the same or similar properties as the glass to be ground.

12. A process according to any preceding Claim, further comprising the step of heating the freeze-dried glass powder for from 1 hour to 10 days in an oxidising atmosphere at a temperature of from 250°C to the glass transition temperature T_g.

13. A process according to Claim 12, wherein the freeze-dried glass powder is heated for from 12 to 48 hours at a temperature of from 400 to 600°C in air.

14. Glass powder when produced by a process as claimed in any preceding Claim.

15. The use of glass powder according to Claim 14 as a filler for plastics.

16. The use of glass powder according to Claim 14 as a

filler for dental plastics.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition K) B2A

(ii) Int Cl (Edition 5) B02C

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES : WPI

Search Examiner

J M WORVELL

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01 APRIL 1992

Documents considered relevant following a search in respect of claims 1-16

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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